#### DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS George K. Burgess, Director

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, No. 259
[Part of Vol. 18]

# SATURATION RELATIONS IN MIXTURES OF SUCROSE, DEXTROSE, AND LEVULOSE

BY

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June 17, 1924



#### PRICE, 10 CENTS

\$1.25 PER VOLUME ON SUBSCRIPTION

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# SATURATION RELATIONS IN MIXTURES OF SUCROSE, DEXTROSE, AND LEVULOSE.

#### By Richard F. Jackson and Clara Gillis Silsbee.

#### ABSTRACT.

The sugars, sucrose, dextrose, and levulose which constitute our adult sugar diet occur in commerce as solids and saturated or nearly saturated sirups. The solubilities of each in the presence of the others have been determined. It is found that invert sugar or dextrose diminishes the solubility of sucrose in water, but that the total sugar content is greatly increased. Similarly, sucrose and levulose diminish the solubility of dextrose. The measurement of the influence of levulose on the solubility of dextrose has made possible a computation of the compositions of invert sugar solutions which are saturated with dextrose. This has been designated the "solubility of invert sugar." The compositions of mixtures of sucrose and invert sugar which are saturated with both sucrose and dextrose at various temperatures have been determined. Such solutions possess the maximum solubilities which may be reached by partially inverted sucrose solutions. Honey has been shown to be a supersaturated solution of dextrose in the presence of levulose and its degree of supersaturation calculated. Various methods of partial inversion of sucrose have been reviewed.

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#### I. INTRODUCTION.

Of the numerous members of the sugar group there are but three which play important parts in adult human nutrition. These are sucrose, dextrose, and levulose. Of these, sucrose and dextrose are consumed as crystalline products or as sirups, while levulose occurs almost exclusively as a sirup mixed with dextrose or with dextrose and sucrose. It is with the sirups containing these mixed sugars that the present article deals. These sirups are, in the manufacturing stages or in the final product, maintained at such high concentrations that they are usually saturated or indeed supersaturated with respect to one or more of the constituent sugars. It is desirable in the preparation of sirups to avoid a degree of supersaturation which causes the deposition of crystals; but, on the other hand, a sirup must have a sufficiently high concentration to be viscous.

A saturated solution of pure sucrose contains at 20° C. 67.1 per cent of sugar. Such a solution possesses too low a density to be useful as a sirup and is, moreover, a favorable medium for the growth of microorganisms. If concentrated to a higher density it may remain supersaturated temporarily, but eventually deposits crystals of sugar. It has been recognized that by partial inversion the total sugar content may be increased without causing supersaturation, but if the sucrose is completely inverted the relatively low solubility of dextrose limits the total sugar content of the sirup. There is, consequently, at each temperature a ratio of sucrose to invert sugar at which the concentration of total sugar attains a maximum. The determination of this maximum solubility is of considerable practical significance.

The problems then are concerned with the solubilities of sucrose and dextrose in the presence of each other and in the presence of invert sugar. Levulose, although rarely appearing as a solid phase, is a constituent of invert sugar and is, moreover, present in honey and similar products. It therefore exerts its influence upon the solubilities in question.

For the solution of these problems it is evidently necessary to make measurements of the solubility of each of the constituent sugars in the presence of varying amounts of each of the others. In other words, we require the phase rule and its systematic method of treatment. We have, therefore, studied the various phase rule systems which are pertinent to the present problem.

#### II. GENERAL DESCRIPTION OF THE SOLUBILITY MEASURE-MENTS.

The solubility measurements were made by inclosing the solution always with a large proportion of the respective solid phase in long narrow flasks fitting in a metal frame which was kept in constant rotation under the water of an electrically operated thermostat. The thermostat, in general, maintained a constancy of temperature within o?oi C.

Many of the solutions reached equilibrium rapidly, but others, particularly those containing a high concentration of levulose, attained it more slowly. The time allowed was never less than three days. For the solutions of greater concentration this period was extended to six or more days, and in a few instances to several weeks. Frequently, after a sample was taken, the flask was closed and allowed to rotate for a further length of time. In most of these instances, the same solubility was indicated after both intervals.

After the flasks had been agitated for the desired length of time, they were removed from the rotating frame and placed upright in a stationary rack attached to the wall of the thermostat. After the solid phase had settled, the clear solution was sampled and analyzed.

From the more concentrated solutions, however, the solid phase separated too slowly to permit the utilization of this method. In its stead, recourse was had to a method of filtration under pressure. For this purpose a filter was constructed which is described in another communication. Briefly, it consisted of an ordinary Wiley filter tube with asbestos mat, such as was formerly used in reducing sugar analysis. The sirup was forced through the filter by means of compressed air.

#### III. THE SYSTEM: SUCROSE, INVERT SUGAR, AND WATER.

The solubility of sucrose in the presence of invert sugar has been studied by Prinsen Geerligs.<sup>2</sup> From a series of measurements, in which sucrose was dissolved in the presence of invert sugar to form supersaturated solutions and subsequently allowed to crystallize, he drew the conclusion that the presence of invert sugar was without influence upon the solubility of sucrose. Since the solutions upon which he experimented remained motionless during the crystallization, it is probable that they were super-

The Solubility of Dextrose in Water, B. S. Sci. Paper No 437, 17, p. 715; 1922.
 Cane Sugar and Its Manufacture, p. 306; 1909. Norman Rodger, Altrincham.

saturated even at the end of one month, the time allowed by Geerligs.

A portion of our measurements on this system was made in 1917.<sup>3</sup> The work was then interrupted and the results were withheld from a more general publication because they were not satisfactorily complete. In the meantime, van der Linden <sup>4</sup> has published his measurements on this system. As will be observed from Figure 2, the two sets of measurements are in approximate agreement.

For the experiments described below the invert sugar was prepared from pure sucrose either by inversion with a minute quantity of hydrochloric acid which was subsequently neutralized or by use of a small quantity of invertase. After completion of the latter inversion the solution was heated to 70 or 80° C. in order to inactivate the enzyme.

#### 1. ANALYTICAL PROCEDURE.

In order to analyze a mixture of two sugars, two equations are required. These were furnished by a determination of the density of the solution and by a direct determination of sucrose by the Clerget procedure.

The sample was transferred to a weighed 100 ml volumetric flask and weighed. It was then dissolved, made to volume at 20°.00 C., again weighed, and the density calculated. All weights were corrected to vacuum. The volumetric flasks possessed long, narrow necks and were frequently calibrated. It was found to be possible to reproduce the calibration well within 0.005 ml. The density determinations of the solutions after dilution of the sirup to the volume of the flask were, therefore, valid to about five units in the fifth decimal.

If, then, we know accurately the relation between the concentration and density of the solution, the data are sufficient for the determination of total solids. From the density of a solution we found what would have been its concentration were the total sugar content sucrose, and what its concentration if invert sugar. Then, knowing approximately the ratio of sucrose to invert sugar, we obtained the percentage of total sugars by interpolating between these two values.

The densities of sucrose solutions of varying concentrations have been accurately determined by Plato.<sup>5</sup>

<sup>&</sup>lt;sup>3</sup> Dissertation, R. F. Jackson, Harvard University; 1917.

<sup>&</sup>lt;sup>4</sup> Arch. Suikerind., 27, pp. 591-598; 1919.

<sup>&</sup>lt;sup>5</sup> B. S. Circular No. 44, p. 137; 1918.

For the densities of invert sugar solutions at 20° we have only the measurements of Ost,6 made in an investigation of their specific rotations. Inasmuch as these densities were of fundamental importance in the present analytical work we have verified and amplified the existing data. The experimental work will be described in a later publication.

In determining sucrose, two modifications of the Clerget method were employed. In the earlier experiments the inversion was accomplished by means of invertase in order to obviate the uncertainty caused by acid in the presence of invert sugar. In these analyses the method and the Clerget constant used were those suggested by Browne.<sup>7</sup> It was at that time verified by analyses of known solutions and found to give accurate results.

Subsequently to the first group of experiments a study was made of the Clerget method<sup>8</sup> by acid inversion and it was found that reliable analyses could be obtained if the direct polarization was made in the presence of a weight of sodium chloride equal to that of the hydrochloric acid used for the invert polarization. In all the later experiments, the solutions, notably those containing a high concentration of invert sugar, were analyzed by this method.

#### 2. EXPERIMENTAL RESULTS.

The solubilities of sucrose at 23°15, 30°0, and 50°0 C. in the presence of varying amounts of invert sugar, as shown by these measurements, are summarized in Tables 1, 2, and 3 and plotted in Figure 1 (curves AC, MN, and OQ). The solubilities calculated to a constant water content are plotted in Figure 2. In Figure 2 are plotted also van der Linden's values. While the general agreement between the two sets of observations is satisfactory, systematic differences are observable, particularly in concentrated solutions and especially at 50° C. In columns 4 of Tables 1, 2, and 3 are recorded the weights of sucrose which are dissolved by 100 g of water containing varying weights of invert sugar, and in columns 5 the true purity of the sirup.

The results show that invert sugar causes a marked reduction in the solubility of sucrose.

The lines AJ, MJ, and OJ in Figures 1 and 2 are the loci of all solutions having a constant ratio of sucrose to water. In order to avoid confusion in Figure 1 only the line AJ has been drawn.

<sup>6</sup> Ber. Chem. Ges., 24, p. 1636; 1891. Landolt u. Börnstein Tabellen, p. 309; 1912.

<sup>&</sup>lt;sup>7</sup> J. Assoc, Off. Agric, Chem., <sup>2</sup>, No. <sub>3</sub>, p. 139, 1916; B. S. Circular 44, p. 175, 1918. <sup>8</sup> B. S. Sci. Paper No. 375, 16, p. 125; 1920.

The positions of the lines MJ and OJ may be readily located by means of a straight edge. The departure of the solubility curves from these lines shows graphically the salting-out effect of invert sugar. This salting-out effect occurs as one of the factors in cane molasses formation.

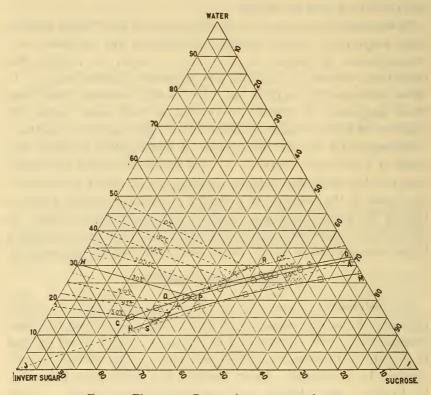


Fig. 1.—The system: Sucrose, invert sugar, and water.

MN, AC, and OQ are saturation curves of sucrose in the presence of invert sugar. HP is the composition of invert sugar saturated with dextrose in the presence of sucrose. P is the composition of a mixture of sucrose and invert sugar saturated with sucrose and dextrose at 30° C. RS represents the variation of P with temperature. Solid lines are experimental; dotted are computed.

TABLE 1.—The System: Sucrose, Invert Sugar, and Water at 23°15 C. with Sucrose as the Solid Phase.

| Invert sugar.                                | Sucrose.  | Invert<br>sugar<br>on 100 g<br>water. | Sucrose<br>on 100 g<br>water.            | Purity.  |
|--|---|---------------------------------------|--|--|
| Per cent.<br>0<br>11. 90<br>25. 39<br>36. 90 | Per cent.<br>67. 59<br>57. 84<br>47. 31<br>38. 66 | g<br>0<br>39. 32<br>93. 00<br>150. 98 | 208. 55<br>191. 14<br>173. 30<br>158. 18 | Per cent.<br>100. 00<br>82. 94<br>65. 08<br>48. 84 |

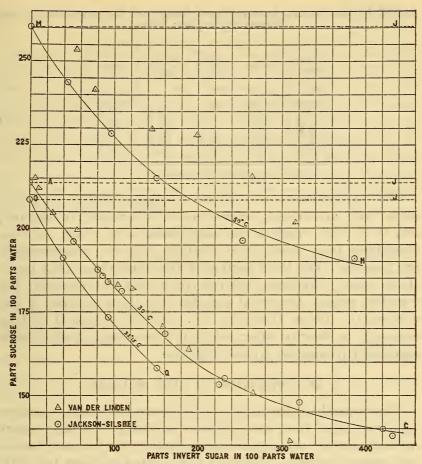


Fig. 2.—The saturation curves of sucrose in the presence of invert sugar, plotted with respect to a constant weight of water.

TABLE 2.—The System: Sucrose, Invert Sugar, and Water at 30°0 C. with Sucrose as the Solid Phase.

| Invert sugar.   | Sucrose.   | Invert<br>sugar<br>on 100 g<br>water.   | Sucrose<br>on 100 g<br>water.  | Purity.  | D 30° C.  |
|---|--|---|--|--|---|
| Per cent. 0 14. 94 21. 86 23. 21 24. 46 24. 52 28. 51 37. 48 47. 02 47. 62 56. 37 63. 68 64. 47 | Per cent. 68. 11 56. 32 50. 97 49. 91 48. 95 48. 93 46. 36 39. 23 32. 06 31. 85 26. 03 21. 18 20. 59 | g<br>0<br>51. 98<br>80. 46<br>86. 34<br>91. 99<br>92. 25<br>109. 29<br>160. 93<br>224. 76<br>231. 95<br>320. 28<br>420. 61<br>431. 52 | g<br>213. 58<br>195. 96<br>187. 60<br>185. 68<br>184. 09<br>184. 29<br>180. 88<br>168. 43<br>153. 25<br>155. 13<br>147. 90<br>139. 89<br>137. 82 | Per cent.<br>100. 00<br>79. 03<br>69. 98<br>68. 25<br>66. 62<br>62. 34<br>51. 14<br>40. 54<br>40. 08<br>31. 59<br>24. 96<br>24. 21 | 1. 3301<br>1. 3485<br>1. 3571<br>1. 3587<br>1. 3608 |

TABLE 3.—The System: Sucrose, Invert Sugar, and Water at 50°0 C. with Sucrose as the Solid Phase.

| Invert sugar. | Sucrose.  | Invert<br>sugar on<br>100 g<br>water. | Sucrose<br>on 100 g<br>water. | Purity.   |
|---------------|---|---------------------------------------|-------------------------------|-----------|
| Per cent.     | Per cent. 72. 25 62. 81 53. 80 46. 20 35. 75 28. 18 | g                                     | g                             | Per cent. |
| 0             |   | 0                                     | 260, 36                       | 100, 00   |
| 11. 42        |   | 44. 31                                | 243, 73                       | 84, 62    |
| 22. 65        |   | 96. 17                                | 228, 45                       | 70, 37    |
| 32. 32        |   | 150. 46                               | 215, 08                       | 58, 84    |
| 46. 05        |   | 253. 02                               | 196, 43                       | 43, 70    |
| 1 57. 06      |   | 386. 4                                | 190, 8                        | 33, 06    |

<sup>&</sup>lt;sup>1</sup> Mean of four concordant determinations.

The measurements are carried to concentrations of invert sugar which are strongly supersaturated with respect to dextrose, and it is only owing to the sluggishness with which dextrose crystallizes from invert-sugar solutions that the measurements are possible. The lower portion of the curve, then, is in a metastable state. Obviously, this one curve does not represent the complete system, because it includes only the solubilities of one component. Before discussing the complete system it will be necessary to describe other solubility determinations which were necessarily preliminary to its completion.

#### 3. AN APPLICATION TO CANE MOLASSES.

The proposal has been made and seriously discussed to remove the invert sugar from cane molasses by means of certain yeasts or moulds which are capable of fermenting the hexoses, but do not secrete invertase. Browne <sup>9</sup> has pointed out that but little advantage would accrue from this procedure, the net result being merely a transformation from a molasses of the cane type to one of the beet type.

It is apparent from the solubility relations described above that we must draw an even more adverse conclusion. Thus, in an exhausted cane molasses of high reducing sugar content, the sugar solubility is a function of two opposing influences, namely, the tendency of the salts to retain an excessive amount and the tendency of the reducing sugar to salt out a portion of the sucrose. Evidently the removal of the invert sugar by fermentation would leave a residue which was already more exhausted than could have been obtained in the absence of invert sugar.

<sup>9</sup> Browne, Handbook of Sugar Analysis, p. 651; Wiley and Sons (Inc.), 1912.

# IV. THE SYSTEM: SUCROSE, DEXTROSE, AND WATER AT $30^{\circ}$ C.

Frequently sirups derived from cane juices contain dextrose and levulose in unequal proportions. This arises from the fact that one or the other of the constituents of invert sugar may undergo a partial elimination by the action of defecating chemicals, microorganisms, possible selective absorption by decolorizers, or by the destructive effect of high temperatures. Consequently, it is of practical importance to determine the effect of dextrose alone upon the solubility of sucrose. In the case of dextrose, the complete series ranging from the solubility of pure sucrose to that of pure dextrose is described.

#### 1. ANALYTICAL PROCEDURE.

The analysis of dextrose-sucrose mixtures was accomplished by a determination of the total solids by a densimetric measurement and a direct determination of sucrose by the Clerget method. For the density of dextrose solutions the determinations made by Jackson <sup>10</sup> were used.

The modification of the Clerget method which we employed was that suggested by Browne.<sup>11</sup> These measurements were made in 1917, at which time our own modification of the Clerget method had not been developed. As Browne has shown, the presence of pure dextrose has no disturbing influence on the Clerget method. The direct polarization was made on a pure neutral solution of the weighed sample made up to 100 ml. For the invert polarization, 50 ml of this solution was made up to 55 ml with concentrated hydrochloric acid and again made to the same volume after inversion overnight at room temperature.

#### 2. EXPERIMENTAL RESULTS.

The solubility measurements on the complete system at  $30^{\circ}$  C. are assembled in Table 4 and plotted on curves AD and ED in Figure 4. A striking feature, which may be seen readily in Figure 4, is that the solubility of sucrose in the presence of dextrose is almost coincident with its solubility in the presence of invert sugar. In other words, invert sugar, dextrose, and, consequently, levulose exert almost exactly the same influence upon the solubility of sucrose. They all exert a salting-out effect, a diminution of the solubility of sucrose in the water. In fact,

<sup>10</sup> B. S. Bull., 13, p. 642, 1916; B. S. Sci. Paper No. 293.

<sup>11</sup> J. Assoc. Off. Agric. Chem., 2, p. 136, 1916; B. S. Circular 44, p. 174, 1918.

these substances serve as exact examples of the term "negative" molasses formers." Similarly, sucrose diminishes the solubility of dextrose.

The relatively low solubility of dextrose limits the length of the sucrose solubility curve, and at the concentration, 49.70 per cent sucrose, 25.60 per cent dextrose, we arrive at the quadruple point D, in which the two solid phases, sucrose and dextrose hydrate, are in equilibrium with the same solution and vapor. The left-hand limb shows the solubilities of dextrose in the presence of sucrose, the solid phase being, at all concentrations, dextrose with one molecule of water of crystallization.

Pure white sugar solutions find considerable application in the arts. Evidently it is possible to prepare a saturated sirup, containing the mixed sugars, of much higher concentration than one containing sucrose alone. At 30° 100 g of water dissolve 213.6 g of sucrose, but 280.1 g of the two sugars mixed, an increase of 31 per cent. Since both sugars are abundant commercial commodities such a mixed sirup may find application where a concentrated solution is desirable.

#### 3. APPLICATION TO MOLASSES.

It has been proposed in technical and in patent literature to add dextrose to exhausted molasses in order to obtain by its salting-out effect a further crystallization of sucrose. From the data in Table 4 we are enabled to compute the approximate efficiency of this process. The assumption is necessary that the process is so conducted that the total amount of water in the molasses remains constant, or, in other words, that anhydrous dextrose is dissolved directly in the molasses.

| TABLE | 4.—The | System: | Sucrose, | Dextrose, | and | Water | at 30° | C. |
|-------|--------|---------|----------|-----------|-----|-------|--------|----|
|-------|--------|---------|----------|-----------|-----|-------|--------|----|

| Solid phase.                    | Sucrose.                                 | Dextrose.  | Sucrose<br>on 100 g<br>water.                            | Dextrose<br>on 100 g<br>water.                      | D 30° C.  |
|---------------------------------|--|--|--|---|---|
| Sucrose                         | Per cent.  68.11 64.22 60.40 53.19 48.60 | Per cent.<br>0<br>4.89<br>9.70<br>18.58<br>24.61 | g<br>213. 58<br>207. 90<br>202. 07<br>188. 41<br>181. 41 | g<br>0<br>15. 83<br>32. 45<br>65. 82<br>91. 86      | 1. 3301<br>1. 3356<br>1. 3411<br>1. 3507<br>1. 3588 |
| Sucrose and hydrated dextrose 1 | 47. 10<br>33. 79<br>19. 66<br>7. 35<br>0 | 26. 59<br>33. 88<br>41. 97<br>50. 00<br>54. 64   | 179. 02<br>104. 51<br>51. 24<br>17. 23                   | 101. 06<br>104. 79<br>109. 38<br>117. 23<br>120. 46 | 1. 3227<br>1. 2867<br>1. 2592<br>1. 2434            |

<sup>&</sup>lt;sup>1</sup> This point is the quadruple point D in Figure 4.

In columns 4 and 5 of Table 4 we find that r g of dextrose added to a saturated solution of sucrose in 100 g of water salts out an average of 0.37 g of sucrose at 30° C. It would, therefore, require about 3 pounds of anhydrous dextrose to obtain 1 pound of sucrose. In order to carry out the process in this way the density of the massecuite would have to be increased by a relatively large amount for each unit of sucrose obtained. The alternative process of maintaining the total solids in constant percentage by adding aqueous dextrose of the same percentage composition as total solids in the molasses would yield no sucrose at all, for we would then be merely transferring our concentrations, as can readily be seen in Figure 4, to the region of unsaturation. For the above-described process to be a practical and economic success, anhydrous dextrose must be provided at less than onethird of the cost of sucrose and the crystallization must be carried out at much greater densities than is now customary.

#### V. THE SYSTEM: DEXTROSE, LEVULOSE, AND WATER.

A complete record of the mutual solubilities of the three sugars with which we are concerned must include the influence of the presence of levulose as well as sucrose upon the solubility of dextrose, since dextrose may readily crystallize from an inverted solution.

These determinations were made in the manner described above. The solid phase, which was pure hydrated dextrose, was always present in large excess. The equilibrium in the presence of large quantities of levulose was slow of attainment and thus the solutions were given long periods of agitation. The levulose was added in the form of invert sugar prepared from sucrose by use of invertase. For the solutions of high levulose content, invert sugar in concentrated solution was allowed to stand until considerable dextrose had crystallized out.

#### 1. ANALYTICAL PROCEDURE.

The two equations necessary for the analysis were constructed from the densities of the solution and the rotary power. For the densities of levulose solutions, the work of four authors <sup>12</sup> is available, three of which are in satisfactory agreement. These data were combined and the average densities employed.

<sup>18</sup> Landolt u. Börnstein Tabellen, p. 308; 1912.

The rotary power of pure levulose is not known with sufficient accuracy for the present purpose. Its rotation on the quartzwedge saccharimeter has never been determined, and, moreover, with our insufficient knowledge of the rotation of sugar mixtures. it would be hazardous to apply any selected value to the rotation of levulose in the presence of a large amount of dextrose. Consequently, an empirical equation which is suitable only for the present purpose was constructed.

The method of calculation depends on the assumption that the specific rotations of each of these sugars is constant in a constant concentration of total sugar, or, in other words, in a constant concentration of water. This fact was first shown by Rosanoff, Clark, and Sibley 13 and found to be very nearly true by the authors 14 in a previous communication. More recently this principle has been shown to be true in certain instances by Vosburgh. 15 The equation embracing the resultant rotary power of the mixture was of the form Ax + By = R, in which x and y are the number of grams of dextrose and levulose, respectively, in 100 ml. A and B are the saccharimetric rotations produced by I g of each of the sugars, respectively, in the concentrations of total sugars with which we were concerned in these measurements. The values of A and B were computed for each per cent concentration of constant total sugars from 18 to 22 per cent. The values of A were found from the measurements made by Jackson 16 on pure dextrose. The values By, and thus of B, were found by subtracting the values of Ax from the rotations of pure invert sugar solutions. The latter are known accurately from the determinations of Browne, 17 and were corroborated by the present authors in a previous communication. Having determined the constants in the equation, a known mixture intermediate between dextrose and invert sugar was prepared and the method found to be sufficiently accurate.

#### 2. EXPERIMENTAL RESULTS.

The solubilities thus determined are summarized in Table 5 and plotted in curve EG in Figure 3. The curve shows that a relation similar to that of the other combinations exists.

<sup>13</sup> J. Amer. Chem. Soc., 33, p. 1924; 1911.

<sup>&</sup>lt;sup>14</sup> B. S. Sci. Paper No. 375, 16, p. 173; 1920.
<sup>15</sup> J. Amer. Chem. Soc., 43, p. 219; 1921.

<sup>16</sup> B. S. Bull., 13, p. 633, 1916; B. S. Sci. Paper No. 293.

<sup>&</sup>lt;sup>17</sup> J. Assoc. Off. Agric, Chem., 2, p. 134, 1916; B. S. Sci. Paper No. 375, 16, p. 167, 1920.

presence of levulose decreases the solubility of dextrose. The salting-out effect of levulose is seen to be slightly less than that of sucrose.

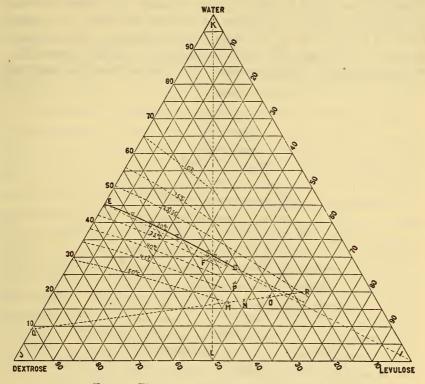


Fig. 3.—The system: Dextrose, levulose, and water.

EG is the saturation curve of dextrose in the presence of levulose determined experimentally. The dotted curves extending from the KJ coordinate are similar curves computed. The line KL is the locus of invert sugar solutions. The intersections of the dextrose saturation curves with KL represent the compositions of invert sugar solutions saturated at the respective temperatures with dextrose. M, alfalfa honey; N, sage honey; O, tupelo honey; P, Cuban honey.

TABLE 5.—The System: Dextrose, Levulose, and Water at 30° C. with Hydrated Dextrose as the Solid Phase.

| Dextrose.   | Levulose.   | D 30° C.                                 |
|---|---|--|
| Per cent.<br>54. 64<br>49. 34<br>49. 32<br>45. 97<br>41. 01 | Per cent.<br>0.00<br>8.94<br>8.94<br>14.50<br>23.23 | 1. 2639<br>1. 2650<br>1. 2779<br>1. 3000 |
| 35. 76<br>34. 48<br>33. 67<br>32. 55                        | 33. 09<br>35. 69<br>37. 10<br>39. 39                | 1. 3286<br>1. 3359<br>1. 3408<br>1. 3480 |

#### 3. "SOLUBILITY" OF INVERT SUGAR AT 30° C.

If the triangular diagram, Figure 3, is bisected by the line KL drawn from the vertical apex to the center of the base, KL is the locus of all solutions in the dextrose, levulose, and water system, in which the ratio of dextrose to levulose is unity. In other words, it is the locus of all invert sugar solutions. At the intersection F of the line KL with the dextrose solubility curve EG, we have the point which represents the composition of a solution

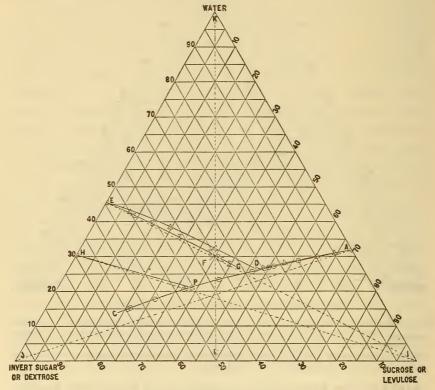


Fig. 4.—Summary of saturation relations at 30° C.

⊙, the system: Sucrose, invert sugar, and water. △, sucrose, dextrose, and water. ☒, dextrose, levulose, and water.

which is saturated with dextrose and which contains 34.85 per cent of dextrose and 34.85 per cent of levulose. In other words, this point represents the "solubility" of invert sugar, if "solubility" is understood to have the significance given above. Our conclusion is that a solution containing 69.7 per cent of invert sugar is saturated at 30° C. with respect to dextrose.

For the purpose of a phase rule diagram, the solubility of invert sugar as thus defined has a definite significance. Invert sugar may properly be considered a component, provided the constituents are not independently variable. The constituents are, of course, variable for concentrations at which dextrose is capable of crystallizing, but as long as they are not varied, but are arbitrarily kept constant, we may properly plot the solubility curve of invert sugar, provided we keep in mind the restrictions which the term "solubility" implies.

Having found that the solubility of invert sugar is 69.70 per cent, we may now plot this as a point on the sucrose-invert sugar diagram, Figures 1 and 4. This is represented by the point H.

#### 4. "SOLUBILITY" OF INVERT SUGAR AT VARIOUS TEMPERATURES.

An inspection of the curve EG in Figure 3 shows that the solubility curve of dextrose in the presence of levulose departs but slightly from the line EI. This indicates that the salting out effect of levulose is small. If we know, therefore, the solubilities of dextrose in pure water we may, by assuming that this effect is approximately the same at other temperatures, construct a table of the solubilities of dextrose in invert sugar at various temperatures. In a previous paper 18 we have published the solubility measurements of pure dextrose in water as a function of temperature. These solubilities are reproduced in Table 6. By plotting these values on the line JK of Figure 3, connecting these points, respectively, with the point I by straight lines and by estimating the departure of the solubility curves from this linear relation, we obtain an approximate measure of the saturation concentration of dextrose in invert sugar solutions. These values, which are given in Table 6, are probably accurate to about five units in the first decimal.

TABLE 6.—Approximate Composition of Invert Sugar Solutions Saturated with Respect to Dextrose at Various Temperatures (Computed).

| Tempera-<br>ture.                            | Dextrose<br>in water.1                                  | Composition of invert sugar solutions saturated with dextrose. |
|--|---|--|
| ° C.<br>0<br>10. 0<br>15. 0<br>20 0<br>25. 0 | Per cent.<br>35. 0<br>40. 8<br>44. 0<br>47. 2<br>50. 80 | Per cent. 50. 8 56. 6 59. 8 62. 6 66. 2                        |
| 30. 0<br>35. 0<br>40. 0<br>45. 0<br>50. 0    | 54. 64<br>58. 02<br>61. 87<br>65. 71<br>70. 91          | <sup>2</sup> 69. 7<br>72. 2<br>74. 8<br>78. 0<br>81. 9         |

<sup>&</sup>lt;sup>1</sup> B. S. Sci. Paper No. 437. <sup>2</sup> Determined experimentally.

<sup>18</sup> B. S. Sci. Paper No. 437, 17, p. 715; 1922.

#### 5. HONEY.

Honey is the nectar and saccharine exudations of plants gathered, modified, and stored in the comb of honeybees. In general, floral nectar is a dilute solution containing sucrose, dextrose, and levulose in which sucrose usually predominates. The nectar is gathered and while in the honey sac the sucrose is inverted by an enzyme secreted by the bees. The evaporation of the water is effected by air currents produced by the fanning of their wings. The final product is thus mainly a sirup of dextrose and levulose, with traces of ash, formic acid, nitrogenous substances, dextrin, and other organic nonsugars. Since the ash amounts to from 0.05 to about 0.4 per cent we may safely neglect its melassagenic action. Honey is, therefore, directly comparable with the dextrose levulose system described above.

We have available an extensive series of analyses of American honey published by C. A. Browne <sup>19</sup> and a similar series by A. H. Bryan <sup>20</sup> on imported honey which enable us to make this comparison.

In the following calculations the asn, oextrin, and nonsugars were assumed to be without appreciable influence on the solubility of dextrose. The sucrose which was present in relatively small amount was added arithmetically to the levulose to give the sum of nondextrose sugars. Sucrose in small quantities, as will be seen by inspection of Figure 4, plays very nearly the same rôle in the presence of the solid phase, dextrose, as does levulose. The sum of the water plus total sugars, thus giving the percentage of pure sugar sirup in the honey, in general, amounts to 93 to 98 per cent. The saccharine constituents were converted to a percentage basis of the pure sirup by dividing the analytical data by the respective percentage of the sirup in the honey; that is, 93 to 98, respectively. The three components, dextrose, levulose plus sucrose, and water, for the several characteristic groups of honeys are given in columns 9 to 11 in Tables 7 and 8 and in a few instances are plotted in Figure 3.

If we assume that honey in commerce is stored at a temperature of 23° C., it appears at once that all the honeys analyzed by Browne and by Bryan are supersaturated with respect to dextrose. This corresponds with the familiar observation that dextrose frequently crystallizes even to the point of complete

<sup>19</sup> Chemical Analysis and Composition of American Honeys, Bur. Chem. Bull. No. 110; 1908.

<sup>&</sup>lt;sup>20</sup> Chemical Analysis and Composition of Imported Honey from Cuba, Mexico, and Haiti, Bur. Chem. Bull. No. 154; 1912.

solidification. It is, however, also apparent that even the honeys which do not granulate, such as sage and tupelo honeys, and the very fluid imported honey, are still highly supersaturated at 23° C. The lack of granulation in the high levulose honeys must be ascribed to the sluggishness with which dextrose crystallizes from solutions of high levulose content. This fact corresponds to our experience with such solutions. In fact, the relatively short range of the curve EG in Figure 3 was due to the great experimental difficulty in effecting the equilibrium.

From the aqueous solutions of dextrose at ordinary temperatures the monohydrated form crystallizes. If, therefore, we draw a line from the supersaturated honey to the point which represents the composition of solid dextrose hydrate and produce this line to the saturation curve, we obtain the locus of the concentrations through which the residual sirup passed during the crystallization. At the intersection of the line with the solubility curve at 23°C. we have the composition of the sirup at its saturation point. We may, therefore, calculate the degree of supersaturation existing in the various honeys of which we have the chemical analysis. An example will suffice to indicate the method of calculation.

In the average composition of the pure sugar sirup in the alfalfa honey there are 16.89 per cent water and 37.57 per cent dextrose. Plotting this point on Figure 3 and completing the tie line QR, we find that such a solution brought to equilibrium with dextrose hydrate would contain 19.8 per cent water and 18 per cent dextrose (anhydrous). The crystallized dextrose has, however, carried with it one-tenth of its weight of water as water of crystallization. Thus, if we assume that we have started with 100 g of the original honey, and we let x represent the weight of dextrose dissolved by the remaining water after equilibrium is established

$$\frac{16.89 - 0.1 (37.57 - x)}{x} = \frac{19.8}{18.0}$$

in which both terms represent the ratio of water to dextrose under equilibrium conditions at 23° C.

We find in this manner that there would remain at equilibrium 13.13 g of dissolved dextrose. The original honey had, therefore, a supersaturation coefficient of  $\frac{37.57}{13.13} = 2.86$ . These coefficients are given in the final columns of Tables 7 and 8.

It will be shown in a later section of this paper that the admixture of sucrose to the mixture of dextrose and levulose produces a sirup of very high total sugar content without causing the supersaturation of any one constituent. Thus, in certain low grades of honey with too strong a flavor, the addition of sucrose would probably serve the double purpose of diluting this objectionable flavor and producing a noncrystallizing sirup. There would consequently become directly available for consumption a large quantity of otherwise unsatisfactory honey which could be sold at a relatively low price.

## 6. A POSSIBLE EMPIRICAL RELATION TO PREDICT GRANULATION IN HONEY.

It would possibly be useful in the honey industry if one could predict the probability that granulation would occur by use of an empirical formula. The following form of equation is suggested in a crude way.<sup>21</sup>

Since, at ordinary temperatures, one part of water holds in solution approximately one part of dextrose, the percentage of dextrose in the honey minus the percentage of water represents the per cent of supersaturated dextrose. The tendency to granulate would be roughly proportional to this quantity. This tendency is inversely proportional to some function of the levulose and we have selected arbitrarily the percentage of levulose itself. Thus

Granulation tendency = 
$$\frac{D-W}{L}$$

in which D, W, and L represent the percentage of dextrose, water, and levulose, respectively. The formula is very evidently a measure of instability.

Browne has classified the honey which he examined in five groups with respect to the degree of granulation, namely, solid, semisolid, slight, very slight, and liquid. The mean value of the quotient from the above formula has proved to be in the respective classes: Solid, 0.48; semisolid, 0.41; slight, 0.41; very slight, 0.39; and liquid, 0.31. While the formula classifies the mean values of the groups satisfactorily there are many individual inconsistencies. Thus, among the 42 solid honeys there are 3 which give quotients below 0.30, and among the 16 liquid honeys there are 4 with quotients above 0.40.

<sup>&</sup>lt;sup>21</sup> The authors have had but little practical experience with honey and offer the above as a possible avenue for others directly engaged in its production.

Unquestionably there is another important variable depending upon the clarity or freedom from possible nuclei which would tend to promote crystallization. This fact becomes particularly apparent when we attempt to apply the same classification to the imported honey. Bryan describes these samples as being "extremely dirty, and containing particles of comb and wax \* \* \* pieces of sticks \* \* \* and dead insects." There would, therefore, be a far more favorable medium in the form of abundant nuclei for the promotion of crystallization. The values of the quotients are in these samples: Solid or semisolid, 0.33; slightly crystalline, 0.28; liquid, 0.26.

Evidently if the formula is to have any validity it must be restricted to materials which are in a similar state of clarity.

TABLE 7.—Supersaturation of American Honey Analyzed by C. A. Browne.

| Let-                          |  |   |                   | Oı   | n origin                   | ıal hon                 | ey.  | On 100 pure sirup.         |                                     | sirup.                     | satura-                        |                         |  |
|-------------------------------|--|---|-------------------|--|----------------------------|-------------------------|--|----------------------------|-------------------------------------|----------------------------|--------------------------------|-------------------------|--|
| tered<br>on<br>Fig-<br>ure 3. | Browne's<br>serial<br>numbers.         | Source.   | Granula-<br>tion. | Wa-<br>ter.                                    | Levu-<br>lose.             | Su-<br>crose.           | Dex-<br>trose.                                 | Wa-<br>ter.                | Levu-<br>lose<br>+<br>su-<br>crose. |                            | Ratio<br>levulose<br>dextrose. | tion<br>coeffi-         |  |
| M                             | 1-8<br>9-23<br>27-30<br>38-45<br>46-49 | Alfalfa<br>White clover<br>Sweet clover<br>Compositae<br>Rosaceae | Solid             | 16. 56<br>17. 64<br>17. 49<br>17. 51<br>16. 87 | 40. 24<br>39. 59<br>41. 31 | 1. 77<br>2. 24<br>1. 90 | 36. 85<br>34. 96<br>36. 78<br>33. 93<br>32. 64 | 18. 64<br>18. 20<br>18. 50 | 44, 41<br>43, 53<br>45, 65          | 36, 95<br>38, 27<br>35, 85 | 1. 15<br>1. 08                 | 2. 46<br>2. 66<br>2. 40 |  |
| N<br>0                        | 56<br>82–83<br>1–92                    | SageTupelo  | slight. Liquid    | 16. 43<br>17. 34<br>17. 70                     | 43. 08<br>48. 61           | 3. 39<br>3. 01          | 31. 44   | 17. 42<br>18. 51           | 49. 26<br>55. 10                    | 33. 32<br>26. 39           | 1. 37<br>1. 97                 | 2.37<br>1.66            |  |

TABLE 8.-Supersaturation of Imported Honey Analyzed by A. H. Bryan.

| 1 1                         | Num-<br>ber                           |                         | 0                          | n origin                     | al hone               | ey.                        | On 1                       | 00 pure                         | sirup.                     | Ratio                             | Super-<br>satura-                        |
|-----------------------------|---------------------------------------|-------------------------|----------------------------|------------------------------|-----------------------|----------------------------|----------------------------|---------------------------------|----------------------------|-----------------------------------|--|
| Lettered<br>on<br>Figure 3. | of<br>sam-<br>ples.<br>ana-<br>lyzed. | Source.                 | Water.                     | Levu-<br>lose.               | Su-<br>crose.         | Dex-<br>trose.             | Water.                     | Levu-<br>lose<br>+su-<br>crose. | Dex-<br>trose.             | levu-<br>lose coeffi<br>dex- cien | tion<br>coeffi-<br>cient<br>at<br>23° C. |
| P                           | 33<br>23<br>16                        | Cuba<br>Mexico<br>Haiti | 21. 07<br>21. 04<br>22. 02 | 40. 84<br>39. 94.<br>40. 39. | 0. 94<br>. 80<br>. 55 | 31. 39<br>32. 72<br>33. 68 | 22. 36<br>22. 26<br>22. 79 | 44. 33<br>43. 11<br>42. 36      | 33. 31<br>34. 62<br>34. 85 | 1.30<br>1.22<br>1.20              | 1. 75<br>1. 84<br>1. 90                  |

#### 7. GLUCOSE SIRUPS.

The familiar corn sirup of commerce contains approximately 35 per cent anhydrous dextrose, as determined by reducing sugar analysis, 44 per cent dextrins and other impurities, and 19 per cent water. The influence of dextrins on the solubility of dextrose is at present of unknown magnitude, but we may make either the assumption that, on account of their probable colloidal

nature, they are without appreciable influence or that for some reason they do affect the true equilibrium solubility, and we may then calculate the supersaturation coefficient with respect to the dextrose in a pure water solution.

Nineteen grams of water dissolve at 20° C. 17.1 g of dextrose, whereas the glucose sirup contains 35 g. The supersaturation is consequently somewhat greater than two. One of three striking conclusions must be drawn. Either the analytical method of determination by alkaline copper is very greatly in error; or the influence of dextrins on the solubility is very great; or the high supersaturation of two is maintained quite indefinitely because of the inability of dextrose to crystallize from a solution of such impurity.

# VI. THE COMPOSITION OF A SIRUP OF MAXIMUM SOLUBILITY.

#### 1. THE COMPOSITION AT 30° C.

Having determined the solubility of invert sugar at 30° C. and knowing the slope of the dextrose-solubility curve in the presence of levulose and of sucrose, we are now in a position to compute the solubility curve of invert sugar in the presence of sucrose. All points on this curve must represent solutions which are saturated with respect to dextrose, and contain dissolved dextrose and levulose in equal quantities, together with varying amounts of sucrose. The end of the curve is reached when the concentration of sucrose is increased to saturation. The solution then will be saturated with respect to both sucrose and dextrose and will, therefore, have the maximum concentration which a sucrose-invert sugar mixture may have and still be permanently stable.

In order to compute the expected solubility curve, the three solutions between F and G were assumed to represent solubilities of invert sugar in the presence of an excess of levulose. The influence of the levulose was then computed in terms of sucrose by comparing the relative effects of levulose and sucrose on the solubility of dextrose. This calculation gave three points on the desired line. This line was then produced to cut AC. This construction obviously yielded only a first approximation, since the extrapolation was considerable, and since any curvature could not be predicted. The computed concentrations were next verified experimentally.

A number of mixtures were prepared of such composition that, when saturated with sucrose and dextrose, they would form a series ranging about the computed point. To each of these were added relatively large quantities of crystalline sucrose and dextrose hydrate. These mixtures were agitated for four days at 30° C., and the saturated sirup sampled and analyzed.

From the direct polarization was subtracted the rotation of sucrose as determined by the Clerget method. The difference then represented the rotation of the reducing sugars, the total amount of which was found by subtracting the sucrose from the total sugars as determined by the density. In one of these solutions the rotation of the reducing sugars corresponded exactly with the rotation of invert sugar at the concentration of total sugars present. This solution was consequently saturated with sucrose and dextrose and contained dextrose and levulose in equal amounts. It was thus the mixture of sucrose and invert sugar which possessed the maximum solubility.

Another of these solutions corrected for a slight excess of levulose led to the same result. The conclusion drawn from these experiments was that a solution containing 33.57 per cent sucrose and 45.44 per cent invert sugar possessed the maximum solubility at  $30^{\circ}$  C. This mixture is represented by the point P in Figures 1 and 4.

It is now of interest to inquire how great an increase in solubility is accomplished by the partial inversion. Pure sucrose has at 30° C. a solubility of but 68.1 per cent; the sirup of maximum solubility contains 79.0 per cent of total sugars. The increase is therefore 10.9 per cent. This method of comparing solubilities, however, is deceptive because the quantity of water is not the same.

The difference may be seen more clearly if the results are calculated to express the relative amounts of total sugars dissolved by a given quantity of water. Thus we find that 100 g of water dissolves 213.6 g of pure sucrose, but at the composition of maximum solubility, the same quantity of water dissolves 376 g of total sugars. The actual solubility is consequently 1.75 times as great.

C. F. Snyder has called to our attention the behavior of a considerable number of commercial sirups which have been submitted to this bureau for analysis. Many of these have deposited sucrose crystals upon long standing. In every instance when this has occurred, the analytical data show that the sirup has a composition lying in the area of supersaturation as shown in Figure 1.

### 2. THE VARIATION OF THE COMPOSITION OF MAXIMUM SOLUBILITY WITH TEMPERATURE.

As we have seen above, dextrose and, consequently, invert sugar have very large temperature coefficients of solubility. Moreover, the solubility of sucrose itself varies considerably with temperature. As a necessary result the composition of maximum solubility will vary with temperature. Although lack of time prevented the direct determination of these variations, we have adequate data for computing them with sufficient accuracy.

We have given in Table 6 the compositions of invert-sugar solutions, which were saturated with dextrose at various temperatures. We may now plot these as points on the sucrose-invert sugar and water system by considering invert sugar as a single component. The experimental data at 30° showed that the effect of sucrose on the solubility of invert sugar followed the general rule and resulted in a slight salting-out effect. By drawing similar lines from the invert sugar solubilities at each temperature to their intersection with the sucrose-invert sugar solubility curve at the same temperature and estimating the salting-out effects, we obtain an approximation to the desired data. Inasmuch as these results are the result of several approximations, they obviously can not be considered data of high accuracy. But since their only significance lies in their practical usefulness and the permissible variation is large, it is deemed that the accuracy is sufficient for the purposes for which it is designed. These computations are assembled in Table 9 and are represented by the line RS in Figure 1.

TABLE 9.—Compositions of Solutions of Maximum Solubility at Various Temperatures (Computed).

| Temper-<br>ature.                                  | Sucrose.  | Invert<br>sugar.   | Water.  |
|--|---|--|---|
| °C.<br>0<br>10<br>15<br>23. 15<br>1 30<br>40<br>50 | Per cent. 43. 7 40. 9 39. 1 36. 3 33. 6 31. 1 27. 7 | Per cent.<br>27. 2<br>31. 8<br>34. 8<br>39. 9<br>45. 4<br>50. 7<br>58. 0 | Per cent. 29. 1 27. 3 26. 1 23. 8 21. 0 18. 2 14. 3 |

<sup>&</sup>lt;sup>1</sup> Determined experimentally.

The saturation curves in Figure 1 enable us to point out some very practical considerations. The points on the line represent the compositions of the solutions of maximum solubility at the respective temperatures. If the manufacturer wishes to prepare

his sirups with the maximum density he should adjust the solutions to contain the proportions of sucrose, invert sugar, and water for the temperature at which the product is expected to be maintained. If, however, sirups of lower density are to be prepared the requirements are less rigorous and the composition may vary within the region of unsaturation as indicated by the curves. For practical purposes a considerable supersaturation is frequently possible without granulation.

#### VII. METHODS OF PARTIAL INVERSION OF SUCROSE.

There are already in existence a number of methods of producing a partial inversion of sucrose, some of which appear to be suitable for commercial processes. A few of these will be briefly described.

#### 1. METHOD IN USE IN TROPICAL AMERICA.

The interesting, although strikingly primitive, process which is in vogue in the island of Barbados is described by Dr. C. A. Browne.22 We quote from Dr. Browne's article, "the expressed juice flows by gravity through a pipe into a sirup house, where it is clarified by heating with a little milk of lime, care being taken to avoid excess. After it has settled, the clear juice is drawn off into the last tayche (open kettle), a bucket of sour cane juice, which has undergone the acetic fermentation, being added from a puncheon in order to give acid enough to invert part of the sucrose. As the juice becomes concentrated, it is ladled into the next tayche, any blanket of impurities being removed by skimmers. More clarified juice is run into the last tayche and the process of skimming and ladling is continued until in the smallest, or first tayche, it has become concentrated to about 42° B. (cold). \* \* \* amount of inversion produced by the acid cane juice is sufficient to prevent crystallization of the sirup; any excess of volatile acid is boiled away in the tayches. The cane sirup, as thus made, has a most agreeable taste and aroma, being entirely free from the objectionable flavors which characterize sirup made with an excess of lime or by the use of sulphur dioxide, hydrosulphites or other chemicals." This method has been further studied in a practical way by Collens and Warneford<sup>23</sup>.

#### 2. INVERSION BY INVERTASE.

Dr. C. S. Hudson,<sup>24</sup> of this bureau, while in the U. S. Department of Agriculture developed to a high degree the theoretical properties and practical utility of invertase, an enzyme readily extracted from yeast by autolysis and subsequent filtration and dialysis. The practical application of Hudson's investigations was delayed for some years owing to the prohibitive cost of invertase. This enzyme is now a commercial product and Hudson's method is undergoing practical trial on a considerable scale by the U. S. Bureau of Chemistry in the cane sirup producing regions of the South. This method of inversion interferes but little with the ordinary process of extraction, and leaves but little impaired the original flavors of the cane juice.

#### 3. INVERSION BY HYDROCHLORIC ACID.

It is frequently desired to prepare an invert sugar sirup or a sucrose-invert sugar mixture from the pure granulated sugar of commerce. In the absence of the inorganic impurities and non-sugars of the original cane juices, hydrochloric acid in very dilute solution effects the inversion readily.

In a previous paper <sup>25</sup> the authors have discussed in detail the rate of inversion of sucrose by hydrochloric acid and have shown the effect of temperature upon this rate over a wide range of temperatures.

Among the reaction velocities measured are those in which the inversion is catalyzed by o.o. N HCl. It was found that at temperatures ranging from 60 to 90° C. the rates of reaction become sufficiently rapid to be readily adaptable to a commercial process. The outline of the method is then to acidify at a temperature of 60 to 90° C. by adding hydrochloric acid to o.o. N and allow the inversion to proceed for a period of time which is a function of the temperature until the desired degree of inversion is obtained. The sirup is then neutralized by the equivalent amount of sodium carbonate.

Table 10 gives the velocity constants at temperatures ranging from 50 to 100° C. In column 3 is given the time required for half inversion, in column 4, for 90 per cent inversion, and in

<sup>&</sup>lt;sup>24</sup> Numerous references, J. Amer. Chem. Soc., 1908 to 1916.

<sup>25</sup> B. S. Sci. Paper No. 375, 16, p. 138; 1920.

column 5, for 99.9 per cent inversion. These values are obtained by solving for the time, t, in the equation:

$$t = \frac{l}{k} \log_{10} \frac{100}{100 - x}$$

in which k is the velocity constant at the temperature at which the inversion is carried out, and x is the percentage of the sugar which it is desired to invert.

TABLE 10.—Time Necessary for Varying Percentages of Inversion with HCl (effectively 0.01 N) as the Catalyzer.

| Temper-<br>ature.       | Velocity<br>constant.1                                      |   |   | Time for<br>99.9 per<br>cent inver-<br>sion. |
|-------------------------|---|---|---|--|
| ° C. 50 60 70 80 90 100 | 0.001145<br>.003806<br>.01182<br>.03303<br>.08922<br>.26797 | Minutes. 262. 9 79. 1 25. 5 9. 11 3. 37 1. 12 | Minutes.<br>873. 4<br>262. 9<br>84. 6<br>30. 3<br>11. 21<br>3. 73 | Hours. 43.5 3.1 4.2 1.5 233.4 211.2          |

<sup>1</sup> Expressed in minutes and decimal logarithms.
2 Minutes.

While our values for the reaction velocities have been determined for o.o. N HCl, they may be computed to lower acidities without appreciable error by considering the velocity proportional to the concentration of acid. Thus, the velocities at 0.005 N HCl will be very closely half those at 0.01 N and the time of reaction twice as great.

In general, it will be found difficult to gauge the velocity of the reaction with sufficient precision to arrive definitely at the point desired, but it should be easily possible to approach it closely enough for practical purposes. If it is desirable, sirups of variable composition may then be mixed for the final product.

At the expiration of the time required for either the partial or complete inversion of the sucrose the acid must be neutralized. This may be accomplished by either sodium carbonate or sodium hydroxide. The choice between these reagents depends upon the rapidity with which they can be mixed with the sugar liquors. If the agitation in the inversion tanks is sufficiently effective it is safe to use the caustic alkali, if not, the carbonate must be employed. Invert sugar, particularly at high temperature, is decomposed by even very dilute alkali with extreme rapidity and consequently any momentary alkalinity in any portion of the

sirup must be avoided.<sup>26</sup> The carbonate is much less destructive, but even with this reagent great caution should be exercised to secure the quickest possible mingling.

For the same reasons the neutralizing reagent must be added in very slightly less than the theoretical quantity. A slight residual acidity is not injurious to the final sirup, but a slight alkalinity causes a continuing decomposition and a darkening in color.

In practice it is feasible to adjust the hydrogen-ion concentration with great precision by means of the sensitive indicators of the sulphone-phthalein group.<sup>27</sup>

# VIII. CHANGE IN VISCOSITY CAUSED BY INVERSION OF SUCROSE SOLUTIONS.

The "body" of a sirup is usually casually gauged by noting the rapidity with which a bubble rises through the liquid when the container is inverted or by the rate of flow of a few drops on a glass plate. It is probably the resultant of a number of properties, among which are primarily the density and viscosity. The density depends upon the concentration and composition. We have shown above the maximum concentration which the sirup may have and have shown that the density is increased by inversion. It now remains to be seen what effect the inversion has upon the viscosity of the sirup.

Winslow H. Herschell, of this bureau, has kindly measured the absolute viscosities of three solutions at 20° C., using the Bingham viscometer.<sup>28</sup>

In preparing these solutions, 85.00 g of pure, dry sucrose was transferred into each of three 100 ml volumetric flasks. To the first was added 0.0482 g of ammonium chloride and pure distilled water to dissolve and make to volume at 20°00 C. To the second and third flasks was added enough water to make solutions of about 90 ml and 1.06 ml of  $N \times 0.849$  HCl. The resulting solutions were thus one hundredth normal with respect to the acid. The second was heated at  $80^{\circ}$  for 9.1 minutes to invert half the sucrose. The third was heated two hours at  $80^{\circ}$  to invert the sucrose completely in accordance with the velocity constants given in Table 10. The acid was then exactly neutralized with the calculated amount of ammonia and the solutions were made to volume at  $20^{\circ}$  C. These three solutions thus contained exactly 85.00 g of sucrose or its equivalent of hydrolyzed products in 100 cc.

<sup>28</sup> B. S. Bull., 14, p. 64, 1917; B. S. Sci. Paper No. 298.

<sup>&</sup>lt;sup>26</sup> B. S. Sci. Paper No. 375, 16, p. 171; 1920.

<sup>27</sup> W. M. Clark, The Determination of Hydrogen Ions, Williams and Wilkins; 1920.

Mr. Herschel found for the viscosities of these three solutions 133.7, 114.4, and 111.3 centipoises for the sucrose, half inverted and invert solutions, respectively. The value in centipoises is very nearly the relative viscosity with respect to water as unity.<sup>29</sup> Thus the sucrose solution is approximately 133.7 times as viscous as water. The invert sugar solution which contains in 100 cc the chemically equivalent weight of invert sugar is but 111.3 times as viscous as water. Thus the division of the sucrose molecule into two smaller molecules reduces the viscosity by about 16.7 per cent.

For purely comparative purposes the small quantity of ammonium chloride (0.0482 g) which was necessarily added to the inverted solutions was also added to the sucrose solution. We were thus obliged to assume that the salt produced the same effect upon the three solutions. The total effect was undoubtedly extremely small, since, as Kanitz 30 has shown, the relative viscosity of a solution as concentrated as N/8 ammonium chloride referred to water at the same temperature is 0.9999. Our solutions were but 0.009 N with respect to ammonium chloride. Consequently, we judged that the assumption was sufficiently safe for comparative purposes.

The comparison just made is based on the assumption that the sucrose and its equivalent invert sugar were contained in the same volume. There occurs, however, a contraction during the process of inversion and consequently it is of practical interest to determine the change of viscosity which actually accompanies the inversion of a given solution under the proviso that no water is added or subtracted. To compute this change, it is necessary to calculate the viscosity of the sucrose solution which on inversion will yield the invert sugar solution whose viscosity we know. This contraction amounts to 0.933 ml. Hence, the solution which contains 85.00 g of sucrose in 100.933 ml is the one whose viscosity we require. Such a solution contains 64.23 per cent sucrose.

Dr. A. Q. Tool, of this bureau, has constructed an interpolation formula which fits satisfactorily the viscosities of sucrose solutions as determined by Bingham and Jackson and also the single determination by Mr. Herschel. By means of this formula he has found that a 64.23 per cent sucrose solution has the viscosity

121.5 centipoises. Thus, the total effect which includes the concurrent effects resulting from a subdivision of the molecule and change of concentration is a change of viscosity from 121.5 to 111.3 centipoises.

The solution which was partially inverted showed a viscosity of 114.4, which is roughly intermediate between the sucrose and totally inverted solutions.

WASHINGTON, February 7, 1924.

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